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Non-Destructive Assay of Ce-144 in Presence of Transuranic Waste

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Abstract

The Ce-144 isotope has been identified as a radionuclide produced in certain Los Alamos National Laboratory plutonium waste streams and thus may need to be quantified when present in reportable quantities for shipment to the Waste Isolation Pilot Plant (WIPP). The most intense gamma ray from Ce-144 was found to be the 133.53 keV peak. At this energy, there were no interfering plutonium or plutonium daughter gamma rays. Furthermore, it was determined that there were no interferences produced by Ce-144 or its progenies that could degrade the plutonium isotopic analysis. At 5% of the total activity per gram of plutonium, the reportable limit, the Ce-144 peak at 133.53 keV will remain above the primary plutonium peak (129.3 keV) for approximately 7 years and remain quantifiable for at least 12 to 13 years from the time the isotope was chemically separated. It is therefore concluded that Ce-144 will be quantifiable whenever it exceeds 5% of the total activity per gram of plutonium, and will not interfere with the non-destructive assay of plutonium isotopic compositions.

1. Introduction

The waste acceptance criteria[1] for the Waste Isolation Pilot Plant (WIPP) require that certain radionuclides be quantified and at least 95% of the total activity in a container be reported. However, some radionuclides may cause interferences with the reportable isotopes or exceed 5% of the total activity but remain below the detectable threshold, resulting in erroneous quantification. Isotopes have been identified in waste streams based on process knowledge and these have been captured in process status (PS) codes. Non-plutonium isotopes that could be in these waste streams were identified from the PS codes and these are tabulated in Table 1. Many isotopes have already been incorporated in the FRAM isotope analysis program[2], but not all. As a result, a study was initiated to complete the analysis of these isotopes. A report summarizing these findings for Ce-144 was recently published in the JNMM[3]; this report summarizes those findings and adds the implementation description.

2. Description and Properties of Ce-144

Cerium is a highly reactive rare earth metal in the lanthanide series of the periodic table. It is used in the nuclear industry and in analytic chemistry laboratories as an oxidizing agent. The Ce-144 isotope is a fission product lying near the high mass maxima of the fission curve[4]. Cerium has several radioactive isotopes ranging from Ce-134 to Ce-144 with decay modes including electron capture and β^- emission. The isotope of importance in the LANL waste stream is Ce-144 with an atomic mass of 143.9 g/mole and a half-life of 284.1 days, decaying via β^- and α particle to Ce-140.

Table 1. Select Radionuclides Derived From Process Status Codes

Radionuclide	Assessed in PC/FRAM?
Am-241	Yes
Am-243	Yes
Ce-144	
Th-232	Yes
U-233	Yes
Np-237	Yes
Cm-244	
Pa-231	Yes
Depleted Uranium	Yes
Th-230	

Ce-144 is important to the NDA measurements because the Ce-144 was originally thought to cause difficulties with the isotopic calculations performed by the FRAM assay system. Further, it had been uncertain if Ce-144 present at 5% of the total activity would be quantifiable.

3. Ce-144 Decay Properties

The Ce-144 decay scheme involves several steps as shown in Figure 1. Ce-144 undergoes radioactive decay with a half-life, T, of 284.1 days via β^- emission to either Pr-144m or Pr-144. The branching ratio to the metastable state Pr-144m, f_{A1}, is 0.0143 and to Pr144, f_{A2}, is 0.9857. Pr-144m decays with a half-life of 7.2 minutes via γ emission to the ground state, Pr-144, which subsequently decays via β^- emission with a half-life of 17.3 minutes to Nd-144. The radioactive decay continues to Ce-140 by α emission with an extremely long half-life, 2.1 x 10^{15} years, stopping at Ce-140, which is stable. The properties[5] of interest for cerium and its progenies are summarized in Table 2.

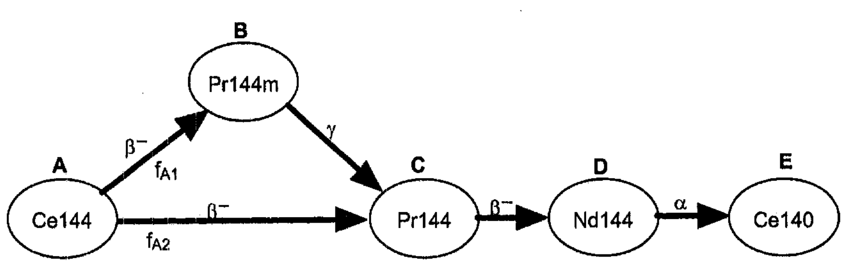

Figure 1. Ce-144 Decay Scheme

3.1. Mathematical Description

The number of atoms, N, of each isotope, subscript A through E (Figure 1), is given by the following solutions to the ordinary differential equations (ODE), where λ (=ln(2)/T) is the decay constant and t the elapsed time following chemical separation.

Table 2. Properties of Ce-144 and Decay Products

Isotope	Half-life, T	Molecular Weight, M (g/mol)
Ce-144	284.144 d	143.914
Pr-144m	7.2 m	143.913
Pr-144	17.283 m	143.913
Nd-144	2.1×10^{15} y	143.010
Ce-140	NA (stable)	139.905

$$N_A = N_{A0} e^{-\lambda_A t} \tag{1}$$

$$N_B = \frac{\lambda_A f_{A1} N_{A0}}{\lambda_B - \lambda_A}\left(e^{-\lambda_A t} - e^{-\lambda_B t}\right) + N_{B0} e^{-\lambda_B t} \tag{2}$$

$$N_C = \frac{\lambda_A N_{A0}}{\lambda_C - \lambda_A}\left(e^{-\lambda_A t} - e^{-\lambda_C t}\right) + N_{C0} e^{-\lambda_C t} \tag{3}$$

$$N_D = \frac{\lambda_A N_{A0}}{\lambda_D - \lambda_A}\left(e^{-\lambda_A t} - e^{-\lambda_D t}\right) + N_{D0} e^{-\lambda_D t} \tag{4}$$

$$N_E = \frac{\lambda_A \lambda_D N_{A0}}{\lambda_D - \lambda_A}\left(\frac{e^{-\lambda_A t}}{\lambda_D} - \frac{e^{-\lambda_D t}}{\lambda_A}\right) + N_{D0}\left(1 - e^{-\lambda_D t}\right) - \frac{\lambda_A \lambda_D N_{A0}}{\lambda_D - \lambda_A}\left(\frac{1}{\lambda_D} - \frac{1}{\lambda_A}\right) + N_{E0} \tag{5}$$

The remaining parameters of interest given by equations (6) through (8) are the activity, A_j, the mass, m_j, and the number of gamma photons per unit time, $\Gamma_{j,k}$, for each isotope, j (j = A, B,...E), and gamma ray peak, k. The gamma ray photon intensity, $I_{j,k}$ expressed as a percent, is the number of gamma photons emitted per 100 disintegrations of the parent nuclide and N^A is Avogadro's number.

$$A_j = N_j \lambda_j = N_j \frac{\ln(2)}{T} \tag{6}$$

$$m_j = \frac{M_j}{\mathrm{N}^A} N_j \tag{7}$$

$$\Gamma_{j,k} = A_j I_{j,k} \tag{8}$$

In a waste matrix containing both plutonium and cerium, the ratio of the activity due to Ce-144 plus its progenies, A_{ce}, to total activity, A, of plutonium and cerium combined is given by equation (9) where A_{pu} is the sum of the activities from all the plutonium isotopes and the plutonium progenies (Am-241, U-237, Np-237, etc.). The equation assumes that there are no other impurities in the waste stream.

$$\frac{A_{ce}}{A} = 1 - \frac{A_{pu}}{A_{ce} + A_{pu}} \tag{9}$$

3.2. Activity in Presence of Plutonium

One gram of typical weapons grade plutonium as exemplified by a PDP[6] standard (Pu-238: 0.0145%; Pu-239: 93.7614%; Pu-240: 5.9445%; Pu-241: 0.2237%; Pu-242: 0.0559%; Am241: 0.00%) will produce 10847 MBq when the material is first chemically separated, that is, time zero. The activity from plutonium and its decay products (including Am-241), A_{pu}, will decay with time. If Ce-144 were present at 5% of the total activity from one gram of weapons grade plutonium, it would represent 570.9 MBq of activity, or 4.83 μg, at time zero. The total isotopic activity from Ce-144 and daughters (A_{ce}) will vary during the period following chemical separation. The activity variation is evident from a plot of the data (Figure 2). The initial activity from Ce (570.9 MBq) will increase to over 1000 MBq very quickly (less than one day) as the Pr-144 builds up. The A_{ce} activity will drop below the initial activity after 9 months following chemical separation (Figure 2 and insert). The activity from Nd-144 is insignificant.

3.3. Gamma Spectrum

The gamma rays[5] from the decay of Ce-144 and daughters are summarized in Table 3. The cerium gamma ray peaks are compared with plutonium (or Pu decay product) peaks for possible interference. The peak at 133.53 keV is interference free, with the closest Pu line at 129.3 keV. The next peak, 146.0 keV, has zero intensity, meaning that its presence is doubtful. The 696.5 keV peak is also interference free with the closest peaks at 662.46 keV and 721.99 keV (Am-241). All the other cerium peaks are at energies not used in quantifying the plutonium isotopics in the current FRAM software. The Cerium and daughter peak energies were also compared to background and no interferences were found using a 15-hour background spectrum. Consequently, Ce-144 and its daughters will not cause any interference with the quantification of the plutonium isotopes.

The most intense gamma ray is at 133.53 keV as shown in Figure 3. The gamma rate from cerium is compared to that from 1 g of weapons grade plutonium using the most intense line (Pu-239 at 129.3 keV) and a rather weak line (Pu-238 at 152.7 keV). The 133.5 keV peak intensity remains above the Pu-238 peak intensity for about twelve years. Beyond twelve years, the gamma rays from all Ce-144 will become extremely weak and the activity will be well below the initial activity and the reportable quantity. Consequently, the ability of the FRAM system to quantify plutonium in the presence of cerium or its progenies will not pose any significant assay problem. Quantities of Ce-144 at or above 5% of the total activity will be detectable using the 133.53 keV line without interference with Pu quantification.

Table 3. Ce-144 and Daughter Gamma Rays

#	Decay	Energy (keV)	Intensity (%)	Overlaps Pu Line?
1	Ce144 → Pr144 or Pr144m	133.530	10.8000	No
2	Ce144 → Pr144 or Pr144m	146.000	0.0000	146.05
3	Pr144m → Pr144	696.490	0.0600	696.6
4	Pr144m → Pr144	814.150	0.0600	813.9
5	Pr144 → Nd144	624.660	0.0010	624.8
6	Pr144 → Nd144	675.020	0.0028	674.2
7	Pr144 → Nd144	696.490	1.4900	696.6
8	Pr144 → Nd144	814.150	0.0028	813.9
9	Pr144 → Nd144	864.530	0.0027	863.6
10	Pr144 → Nd144	1388.000	0.0065	No
11	Pr144 → Nd144	1489.150	0.2960	No
12	Pr144 → Nd144	1562.000	0.0003	No
13	Pr144 → Nd144	2185.610	0.7700	No
14	Pr144 →Nd144	2654.600	0.0002	No
15	Nd144 → Ce140	None	N/A	
16	Ce140	None	N/A	

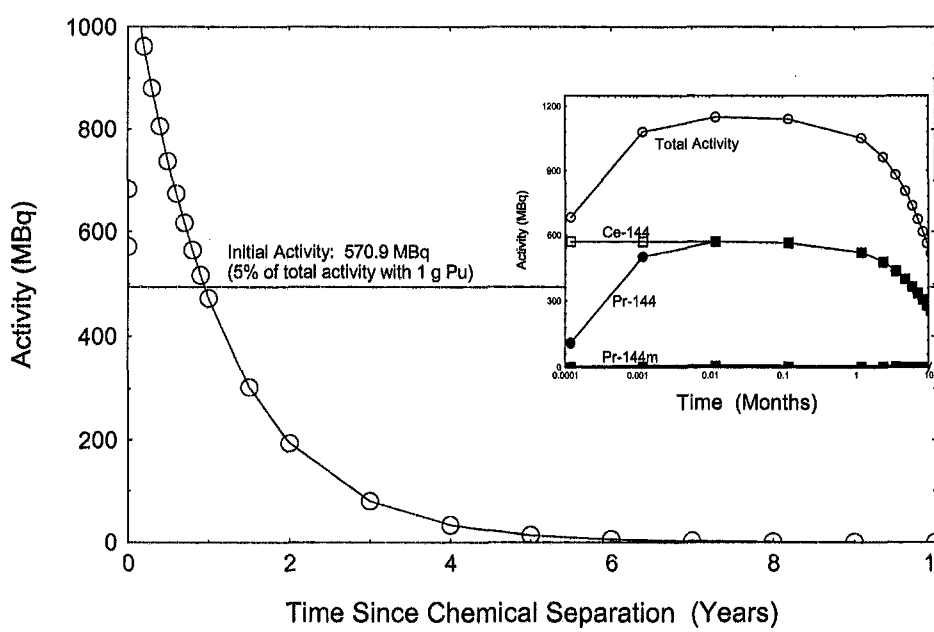

Figure 2. Time To Reduce Ce-144 Activity to Below 5% Total Activity/g Pu

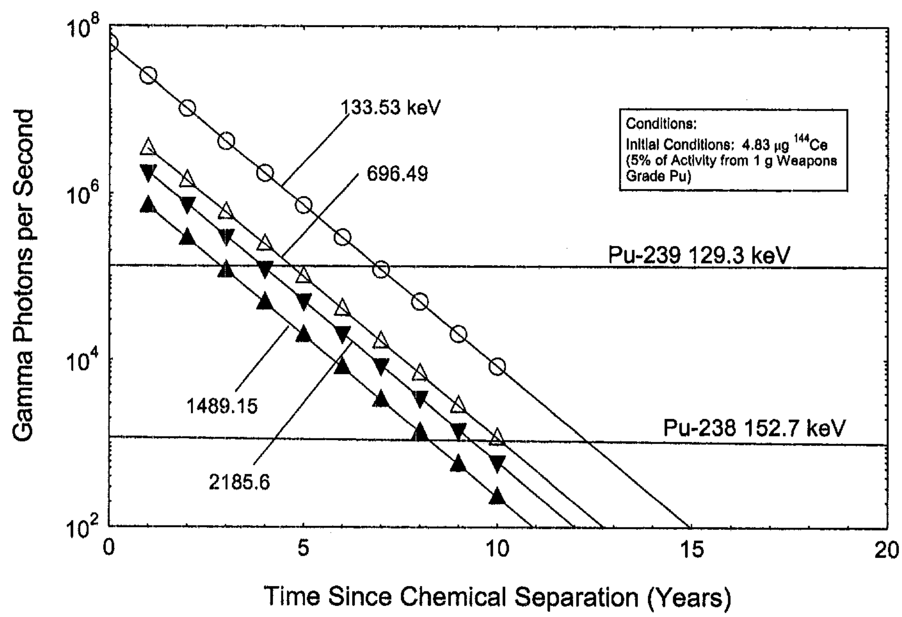

Figure 3. Quantifiable Gamma Ray Lines from Ce-144 or Progenies at 5% Total Activity/g Pu

4. Implementation in FRAM Isotopic Composition Software

FRAM[2] is software designed to analyze gamma spectra and produce isotopic ratios that are subsequently used by quantitative systems. For the Transuranic Waste Certification Program (TWCP) at Los Alamos, it is used to determine the isotopic ratio to plutonium. FRAM requires a "parameter set" that relates the measured signal strength to the anticipated isotopes. The Ce-144 assay was implemented by incorporating the Ce-144 gamma ray at 133.53 keV in the parameter set.

The FRAM assays conducted during 2001 (through May 31, 2001) were evaluated for the Ce-144 response. In all cases, the highest reported ratio of Ce-144 to Pu (1.095×10^{-7}) with the best relative error (27%) was for waste drum 55463 containing approximately 0.9 g Pu. Because the Ce-144 relative error was below the minimum detectable concentration according to Currie[7], the Ce-144 content assayed by the High Efficiency Neutron Counter (HENC) was reported as zero, as shown in Table 4.

The spectrum from the FRAM assay is reproduced in Figure 4 for the region of interest. Two major peaks are observed. The first, at 129.3 keV is the Pu239 peak while the second is a peak consisting of several isotopes. In between these peaks is the region where the Ce-144 signature would appear. As can be seen, there is no visible indication of a peak. The region depicted is where the Ce-144 gamma ray should be observed if present in sufficient mass.

Table 4. HENC Assay Results, Waste Container 55463

Isotope	Activity (MBq)	% Of Total Activity
Pu-238	19.8	0.15%
Pu-239	2009.6	15.14%
Pu-240	389.7	2.94%
Pu-241	5136.2	38.69%
Pu-242	0.0	0.00%
Am-241	2545.4	19.17%
Am-243	66.7	0.50%
Np-237	1.3	0.01%
Ac-227	4.9	0.04%
Cs-137	0.1	0.00%
Ce-144	0.0	0.00%
Pa-231	6.5	0.05%
U-233	0.0	0.00%
U-234	3095.3	23.32%
U-235	0.0	0.00%
U-238	0.0	0.00%
Th-230	0.0	0.00%
Th-232	0.0	0.00%
TOTAL Activity	13275.5	100.00%

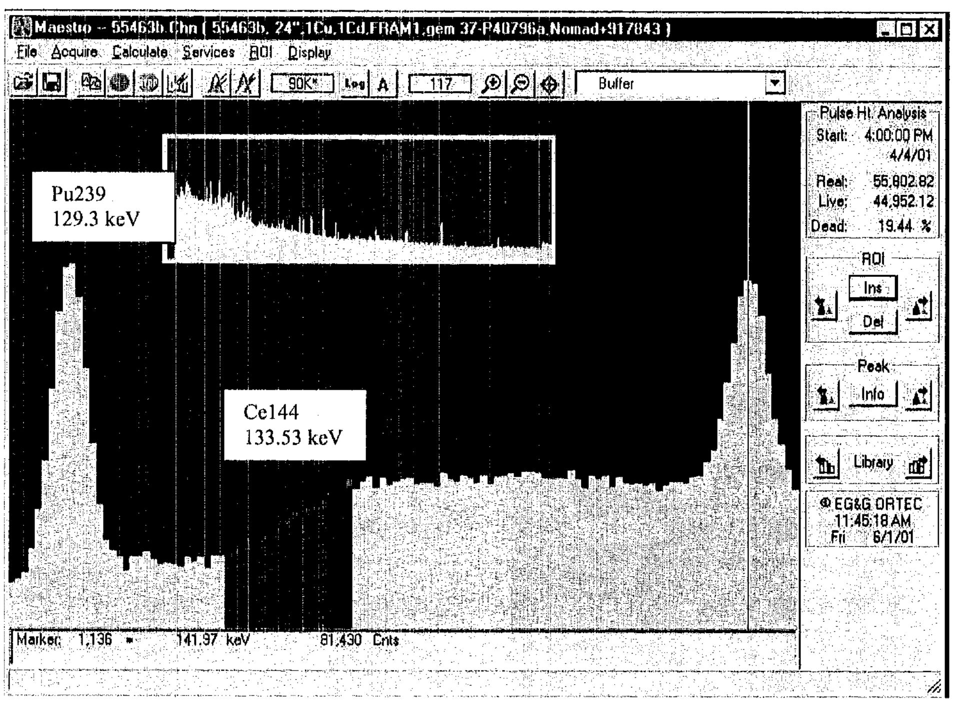

Figure 4. Spectrum of FRAM Assay, Waste Drum 55463

Since the FRAM parameter file implementing Ce-144 was developed in October 2000, no observable Ce-144 signal has been observed through June 7, 2001.

5. Conclusions

Early in the NDA program, the Ce-144 isotope had been identified as a radionuclide that could produce difficulties in the non-destructive assay of plutonium waste. This analysis has shown that Ce-144 will not interfere with Pu assay and that it will be easily detected in quantities exceeding 5% of the total activity.

The decay scheme for Ce-144 was determined and a set of ordinary differential equations derived and solved in order to generate the time-dependent activity and gamma ray emission properties. The most intense gamma ray was found to be the 133.53 keV peak and at this energy, there are no interfering plutonium or plutonium daughter peaks. Furthermore, it was determined that there were no interferences produced by Ce-144 or its progenies that could degrade the plutonium isotopic analysis using current FRAM NDA software. At 5% of the total activity (the current reporting criteria for WIPP) per gram of plutonium, the Ce-144 peak at 133.53 keV will remain above the primary plutonium peak (129.3 keV) for approximately 7 years and remain quantifiable for at least 12 to 13 years from the time the isotope was chemically separated. After this time, the activity from Ce-144 and its progenies will fall well below the WIPP reporting criteria.

It is therefore concluded that Ce-144 will be quantifiable whenever it exceeds 5% of the total activity per gram of plutonium, and will not interfere with the non-destructive assay of plutonium isotopic composition. Through June 2001, Ce-144 has not been observed in the LANL waste streams being assayed by the NDA instrumentation for shipment to WIPP.

REFERENCES

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